Message

From: Dan Pope [DPope@css-inc.com]
Sent: 2/13/2017 3:06:26 PM
To: d'Almeida, Carolyn K. [dAlmeida.Carolyn@epa.gov]; Davis, Eva [Davis.Eva@epa.gov]; Wayne Miller (Miller.Wayne@azdeq.gov) [Miller.Wayne@azdeq.gov]
CC: Henning, Loren [Henning.Loren@epa.gov]
Subject: RE: ST12 EBR RDRAWP RTCS
Attachments: image001.gif

We can come up with our own estimates, but I'm not sure they would be better than their estimates, though probably higher. And I suspect we would then be sitting in interminable meetings arguing about our assumptions for the estimates, etc. Note also that while of course the huge amount of mass is a problem, it's the configuration of that mass that really makes it bad. If the mass were all spread out in tiny globules with lots of water filled effective porosity around them, then EBR would be much more viable for source depletion. But a significant amount of the mass is not like that, which we know because significant mass keeps mobilizing into the wells.

From: d'Almeida, Carolyn K. [dAlmeida.Carolyn@epa.gov]
Sent: Friday, February 10, 2017 11:58 AM
To: Dan Pope; Davis, Eva; Wayne Miller (Miller.Wayne@azdeq.gov)
Cc: Henning, Loren
Subject: RE: ST12 EBR RDRAWP RTCS

AF is already backing off of the 20 year timeframe commitment as a goal, and not a requirement of the RODA but not providing other criteria for evaluating success of the remedy. The objectives of EBR are extremely vague at this point. And if the rate of degradation is less than the rate of transmissivity, a groundwater plume will result unless the area is hydraulically contained for the duration..

Realistically, based upon mass estimates, how many decades (or centuries?) do you think it would take to degrade this much mass? Can we come up with our own range of estimates based upon literature?

From: Dan Pope [mailto:DPope@css-inc.com]
Sent: Thursday, February 09, 2017 5:51 PM
To: d'Almeida, Carolyn K. <dAlmeida.Carolyn@epa.gov>; Davis, Eva <Davis.Eva@epa.gov>; Wayne Miller (Miller.Wayne@azdeq.gov) <Miller.Wayne@azdeq.gov>
Subject: RE: ST12 EBR RDRAWP RTCS

From: d'Almeida, Carolyn K. [mailto:dAlmeida.Carolyn@epa.gov]
Sent: Thursday, February 09, 2017 5:38 PM
To: Davis, Eva; Dan Pope
Cc: Wayne Miller
Subject: ST12 EBR RDRAWP RTCS

What do you think about this response?

Air Force (AF) Response to Comment (RTC) pg 39- 43

The EBR phase of the selected remedy is a source control technology to the extent that it will deplete COCs/COPCs such that groundwater cleanup criteria can be met. The blanket statement that EBR is not a source remedy is not consistent with the state of practice as supported by the following points:

Remember that the problem is not whether EBR could eventually deplete the source material. The problem is that EBR/MNA is proposed to deplete the source material and meet groundwater COC concentration standards within a certain timeframe.

• Source control by bioremediation has been implemented at many sites. Bioremediation is more extensively documented for chlorinated solvent source areas but has also been applied for petroleum hydrocarbon sites. One study for chlorinated solvent sites shows that bioremediation source control performance is competitive and in some cases better than other source control technologies (McGuire et al, 2006).

"Based on current data, none of the 59 source depletion projects was able to meet maximum contaminant levels throughout the treatment zone for all CVOCs." McGuire et al, 2006

• Natural Source Zone Depletion (NSZD) is an established process for LNAPL (ITRC, 2009). Dissolution and biological degradation is one of the primary removal pathways for NSZD. Generally, the timescales of NSZD are not consistent with the timescales in the OU2 RODA 2; however, the proposed approach is designed to accelerate the biological process by providing excess sulfate.

As noted above, the problem is not whether EBR could eventually deplete the source material. The problem is that EBR/MNA is proposed to deplete the source material and meet groundwater COC concentration standards within a certain timeframe.

• Recent developments in NSZD assessment and monitoring consider the use of measuring carbon dioxide (CO_2) flux from above a LNAPL body as a means to quantify its biodegradation rate. Results of CO_2 flux monitoring above LNAPL bodies show that natural biodegradation of LNAPL can be significant; ranging from hundreds to thousands of gallons per acre per year. Under natural conditions, biodegradation

of LNAPL is rate limited based on the flux of TEA.

No one disputes that LNAPL components can be biodegraded.

Note that measuring carbon dioxide flux above a LNAPL body merely gives an index to overall biodegradation going on around the LNAPL body, which would include biodegradation of LNAPL components which are not of regulatory interest.

Within limits, TEA flux is a limiting factor. It is very likely that adding sulfate as a TEA will increase biodegradation of LNAPL components.

• The primary biodegradation pathway is in dissolved phase; however, there is some evidence of direct biological degradation of LNAPL (ITRC, 2009)

D.6 CURRENT UNDERSTANDING OF LNAPL BIODEGRADATION AND ITS ROLE IN NSZD

The literature documents laboratory and field studies that verified direct biodegradation of LNAPL in certain circumstances. However, EPA (1995) states that, while LNAPL constituents are available for biodegradation in the aqueous phase, it is unlikely that conditions exist within an LNAPL that are favorable for biodegradation. The literature above does not necessarily imply that biodegradation is occurring within the LNAPL itself, but rather implies that bio-activity occurs at the LNAPL-water interface (e.g., enzyme secretion and microbial attachment at LNAPL-water interface). While the laboratory studies confirm that biodegradation of LNAPL does occur in some situations and environments, they also point to circumstances that would reduce or eliminate biodegradation of LNAPL. At many environmental remediation sites, in situ conditions may not be conducive to significant direct biodegradation of LNAPL.

Toxicity of certain LNAPLs (e.g., gasoline) to indigenous microbes may serve to minimize or eliminate direct intrinsic biodegradation as a source mass loss mechanism at some sites. It is also possible that indigenous microbes at some sites may be more or less effective at biodegrading the nonaqueous phase. While intrinsic biodegradation of the nonaqueous phase likely contributes to source zone mass loss at many sites, there are no qualitative or quantitative measurements at present that allow independent measurement of the process. Even though direct biodegradation of the nonaqueous phase is not completely understood at this time, the reader should be aware that biodegradation of the LNAPL body likely occurs at many sites. Additional studies of degradation of residual LNAPL have been published by Douglas et al. 1992 and Prince et al. 1994. (ITRC, 2009)

• Dissolution of COCs from residual LNAPL may be the rate limiting step (depletion to the point that rate of remaining LNAPL dissolution does not generate MCL exceedances). The AF expects that, with the establishment of a robust bacteria population, dissolution will be enhanced by concentration gradients and generation of biosurfactants.

"Dissolution of COCs from residual LNAPL may be the rate limiting step"… which is our point, of course. And so the configuration of the LNAPL (which affects the length of the path for diffusion of the COCs from within the LNAPL to the groundwater) is very significant. If LNAPL is present in residual form, in small globules surrounded by flowing groundwater (i.e., on flowpaths where TEA can be moved into proximity to the globules), then movement of the COCs from LNAPL to groundwater, and subsequent biodegradation, could be fairly rapid. If LNAPL is configured in large masses, the diffusion path is long, and transport of COCs from within the LNAPL to the groundwater/LNAPL interface where significant biodegradation can take place takes much more time.

Doubtless "dissolution will be enhanced by concentration gradients and generation of biosurfactants". But by how much? P&T creates concentration gradients too – did it work?

• Sulfate reduction has been observed to be effective at bioremediation of LNAPL associated hydrocarbons (Irianni-Renno et al, 2016). This study points out that "...during the preceding century of LNAPL influence, LNAPL-tolerant microbial communities have been established and microorganisms present readily grow in the presence of LNAPL." Not only are microbes able to biodegrade LNAPL hydrocarbons, they are actively adapting to be more efficient. Irianni-Renno's study also observed metal-sulfide precipitates with no suggestion of deleterious effects.

No one disputes that sulfate reduction can biodegrade LNAPL associated hydrocarbons, including the COCs.

• The notion that bioremediation is not effective on LNAPLs is misleading (Yadav and Hassanizadeh, 2010). In order for bioremediation to occur, the hydrocarbons may need to become solubilized in order to be utilized by microorganisms, so the LNAPL is being degraded, but only after the surface materials partition into solution. Biodegradation rates can exceed advective or dispersive flux thereby driving solubility equilibrium. Also, LNAPL represents the presence of a large electron donor source. As Yadav and Hassanizadeh point out, bioremediation is electron acceptor limited. Because of this, the ST012 site is a uniquely good candidate for the potential success of LNAPL bioremediation due to the high background concentration of sulfate. For bioremediation to be successful, all of the LNAPL does not need to be removed, only enough so that the hydrocarbon flux from the LNAPL is less than or equal to the kinetic capacity of the microorganisms. Yadav and Hassanizadeh point out that the three primary factors that determine the success of LNAPL conditions are: 1) Kinetics (which will be addressed by increasing the sulfate concentration); 2) site-specific conditions (which the field test has shown us to be favorable) and 3) temperature (which is also favorable as a result of the recent SEE operation).

The notion that bioremediation will effectively remove LNAPL so that site remedial goals are met in the limited timeframe might be misleading.

"For bioremediation to be successful, all of the LNAPL does not need to be removed, only enough so that the hydrocarbon flux from the LNAPL is less than or equal to the kinetic capacity of the microorganisms." It depends on what is meant by "success". Remember that we have discussed performance monitoring… where

the monitoring points are located, whether all samples have to consistently meet site goals, etc. As I have stated many times before, EBR/MNA might well be able to control contaminant flux so that downgradient points meet site remedial goals in the remedial timeframe. But if some of the performance monitoring sampling points are located in a subsurface volume with high LNAPL, it could be a very long time before those locations meet site remedial goals.

• LNAPL is a constant hydrocarbon source, creating a concentration gradient on the periphery. Research has shown that chemotactic bacteria will move toward the LNAPL in response to this gradient (Wang et al, 2012).

Microorganisms, like many of the rest of us, love food and move toward it. Development of high populations of sulfate-reducing microorganisms that can degrade the COCs is likely to be fairly straightforward, though creating and maintaining an constant flux of TEA somewhat uniformly to all LNAPL-contaminated points in the subsurface is likely to be challenging.

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"Because a waste is a terrible thing to mind…"